DOCUMENT RESUME

ED 314 095 IR 053 046

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TITLE Artificial Aging as a Predictor of Paper's Future Useful Life.
REPORT NO ISBN-0-9622071-0-1
PUB DATE 89
NOTE 26p.
AVAILABLE FROM Abbey Publications, Inc., 320 Center St., Provo, UT 84606 ($5.00).
PUB TYPE Statistical Data (110) -- Reports - Descriptive (141) -- Reports - Research/Technical (143)
JOURNAL CIT Abbey Newsletter; Monograph Suppl 1

EDRS PRICE MF01/PC02 Plus Postage.
DESCRIPTORS *Archives; Books; Foreign Countries; Library Research; *Paper (Material); *Preservation; Prevention; Scientific Methodology; Statistical Data; Tables (Data); *Thermal Environment; *Thermodynamics
IDENTIFIERS *Artificial Aging of Paper; West Germany

ABSTRACT

An experiment with the artificial aging of paper which--in contrast with the usual practice--was carried out at relatively low temperatures (i.e., 50-95 degrees Celsius), and not on laboratory handsheets, but on naturally aged paper from the commercial production of four centuries, produced results justifying the thesis that there may be at best an accidental agreement between the results of artificial aging at high temperatures and natural aging. The chemical processes that take place as paper ages appear to take different temperature-specific courses, so that it is not possible to draw any conclusions from short-term expiration at one (elevated) temperature about the long-term expiration at another (room) temperature. If artificial aging cannot be dispensed with despite this uncertainty, aging should take place at 80 degrees Celsius and 65% relative humidity. The data collected are displayed in 24 tables and 10 figures. (Author/SD)

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ABBEY NEWSLETTER

Monograph Supplement 1 1989

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IR053046

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THE ABBEY NEWSLETTER

BOOKBINDING AND CONSERVATION

320 E. Center, Provo, UT 84606

Artificial Aging as a Predictor of Paper's Future Useful Life*

by Helmut Bansa and Hans-H. Hofer**

ABSTRACT. An experiment with artificial aging which, in contrast with the usual practice, was carried out at relatively low temperatures (50°C to 95°C), and not on laboratory handsheets, but on naturally aged paper from the commercial production of four centuries, produced results justifying the thesis that there may be at best an accidental agreement between the results of artificial aging at high temperatures and natural aging. The chemical processes that take place as paper ages appear to take different temperature-specific courses, so that it is not possible to draw any conclusions from short-term experation at one (elevated) temperature about the long-term expiration at another (room) temperature. If artificial aging cannot be dispensed with despite this uncertainty, aging should take place at 80°C and 65% RH.

1. Introduction

In the press[1] and in popular scientific[2] as well as archival and library journals of the last 25 years[3] can be found descriptions from archives and libraries of the consequences of the inadequate permanence of modern industrially produced papers. Predictions have been made that a high percentage of the entire book production of the present and the previous centuries will be, in the near future, no longer usable. In contrast to this, it has been variously pointed out[4,5] that the reality of archive and library holdings does not correspond entirely to this assessment. The paper of many (not all) books and documents is poor enough, to be sure, but fortunately the overall picture is not as desolate as those predictions would indicate.

This discrepancy between prognosis and reality has two specific causes. On the one hand, the definition of predicted usability in libraries and archives has been oriented toward the strength requirements of entirely different users of paper, e.g. the packaging and printing industries. Loss of these strength properties has been interpreted as loss of usability in the library and archive. On the other hand, the changes caused in paper by artificial aging, i.e. storage for a short period at elevated temperature, have been equated with changes occurring in storage at room temperature over a longer period. The pertinent measuring and testing criteria have also found acceptance in restoration research and have led there, it seems, to some mistaken and dubious findings concerning the long-term effectiveness of preservation and restoration measures.

Within the context of a larger research project on the science of restoration, which was carried out with help from the Volkswagen Foundation in cooperation with other research organizations at the Institute for Book and Manuscript Restoration of the Bavarian State Library, it was necessary to examine these measuring and testing criteria in more detail, with the aim of defining their relationship to the reality of archives and libraries. A study[6] was published on the realistically objective assessment of the concept of "usability" of aged paper in the archive and library.

In order to evaluate the validity of artificial aging, it was necessary first to review the abundant literature.

2. Previous research

In research, doubt has existed for a long time whether it is permissible to equate changes in paper caused by short-term storage at elevated temperatures with the changes occurring during long-term storage at room temperature.[7,8] An interesting publication[9] has, while affirming the parallel nature of artificial and natural aging, supplied good arguments against this in its tables of measured data. It reports on a 1973 comparison of test data for 36-year-old papers, laboratory handsheets from 1937, with test data for the same papers after artificial aging conducted immediately after production. The ratio between the measured values for alpha cellulose--to point out the greatest discrepancy--can amount to 17.5 or 1.75 or any value in between. The artificial aging undertaken in 1937, if one assumes a parallel between artificial and natural aging as a condition for using the former to indicate the latter, should have changed the paper to an extent corresponding to 36/17.5 = 2 years in the one case, and to 36/1.75 = 20 years in the other. The folding endurance after the artificial aging of 1937 is sometimes higher and sometimes lower than that after natural aging since 1937; from this, one could calculate the 1937 artificial aging as equivalent to both considerably more and considerably less than 36 years of natural aging.

Doubts about the validity of data from artificial oven aging also arise because it is not possible, through such

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*Report on a test carried out at the Institute for Book and Manuscript Restoration [at the Bavarian State Library in Munich] as part of a research project supported by the Volkswagen Foundation on the resistance of paper to aging. [Translated at the Institute for Paper Chemistry from the German ("Die Aussagekraft einer künstlichen Alterung von Papier für Prognosen über seine zukünftige Benutzbarkeit," Restaurator 6: 21-60, 1984, copyright 1984 Munksgaard, Copenhagen), for the Abbey Newsletter. Published here with permission of Munksgaard International Publishers and of the authors.]

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ISBN 0-9622071-0-1

artificial aging, to put the paper into a state equivalent to that of naturally aged papers with regard to a majority of measurable properties. Previous research investigated the conditions of oven aging (temperature and humidity levels) with the aim of finding the most valid ones (one could almost say the "right ones"). It sought better methods of evaluation[10,11] and concerned itself with tests for a variety of characteristics in order to arrive at predictions of the long-term behavior of paper within observable time periods.[12,13,14] The available research results, in spite of their abundance, did not seem adequate for the research project of the Institute for Book Restoration. Previous relevant investigations are marked by the fact that although contradictory recommendations are not lacking,[7,15] aging was almost always conducted at relatively high temperatures. Then, too, the authors worked almost entirely with laboratory hand sheets, not with papers commercially produced for printed books, and not at all with papers that had already seen use. Interesting findings could be expected from analysis of the performance of paper already aged naturally for a longer or shorter period, upon subsequent artificial aging. A further reason why we concerned ourselves at the Institute for Book Restoration with yet another study of artificial aging should not be minimized: we wanted to find a basis for selecting, for our future work, one of the numerous methods recommended in the literature, while discarding the others. Here, a closer investigation of dry oven aging was foregone since the importance of moisture in aging is not only obvious, but is universally acknowledged.

3. Tests

3.1 Papers

The study involved a selection of papers of different age and composition, and of the greatest possible variety. As far as possible, the papers already employed in the earlier study on the concept of usability were selected.[6] Four papers [Nos. 1-4] were new from the mill, and 15 had seen previous use; these 15 previously used papers came from five different centuries. Some characteristics of these papers are found in Table 1. The quality of the papers, according to the earlier study,[6] and their origin, are as follows:

No. 1: Very firm, new woodfree [i.e., free of groundwood] printing paper (Nopaset), 60 g/m², from Nordland Papier GmbH, 2992 Dörpen, FRG

No. 2: Very firm, new woodfree printing paper, 80 g/m², from PWA Grafische Papiere AG, 8201 Raubling, FRG

No. 3: Firm new newsprint paper, 80 g/m², from Haindl Papier GmbH, 8900 Augsburg, FRG

No. 4: Very firm, new woodfree filter paper No. 589² from Schleicher & Schüll, 3354 Dassel, FRG

No. 5: Rag paper, usable with caution: W. Heinsius, Allgemeines Bücher-Lexicon, Leipzig: Brockhaus 1848

No. 6: Very firm, high-quality historical rag paper: Caesar, De bello Gallico..., Florence: Ph. Giunta 1508

No. 7: Quite useful groundwood-containing paper: Die Grosse Politik der europäischen Kabinette 1871-1914, Band 9, Berlin: Deutsche Verlagsanstalt für Politik und Geschichte, 1923

No. 8: Wood-containing paper, fragile in the fold, usable with caution: Katalog der Bibliothek des ... J.J.J. von Döllinger, München: Lindauer 1893

No. 9: Quite useful paper from a cool storage environment, an unused copy of the same publication as No. 8

No. 10: Coated paper from the 1920s, usable without restriction, an unidentified German-Hungarian publication

No. 11: Wood-containing paper, usable without restriction: H. Stegemann, Geschichte des Krieges, Band 2. 111.-120.Tsd. Stuttgart, Berlin: Deutsche Verlagsanstalt 1918

No. 12: Wood-containing paper, no longer usable: Journal des Economistes Série IV tom.26. Paris: Guillaumin 1884

No. 13: Rag paper from the 19th century, no longer usable: Séances et traveaux de l'Académie des Sciences morales et politiques, compte rendu tom. 55. Paris: A. Durand 1861

No. 14: Endangered paper: Jahres-Verzeichnis der an den deutschen Universitäten erschienen Schriften I. Berlin: Asher 1887

No. 15: Wood-containing paper, usable with caution: Ergebnisse der Vitamin- und Hormonforschung I. Berlin: Akademische Verlagsgesellschaft 1938

No. 16: Quite useful paper: Biologisches Centralblatt 26. Erlangen: Besold 1906

No. 17: Historical rag paper, usable without restriction: J.B. Haydt, Kurzer Bergriff ... des Heiligen Nicolai von Tolentin, Ingolstadt: Th. Grass 1694

No. 18: Firm rag paper from the 19th century: Blackwood's Edinburgh Magazine vol. 69 No. 424. London, Edinburgh: Blackwood 1854

No. 19: Firm paper: R. Amundsen, Die Eroberung des Südpols 1. München: Lehmann 1912

No. 20: Firm rag paper from the 19th century: W. Heinsius, Allgemeines Deutsches Bücher-Lexikon Band 3, 1. Leipzig: Brockhaus 1848

No. 21: Rag paper from the 16th century, usable without restriction: Constitutionenes ... in provinciali synodo Salisb. edita. Dillinger: Sebald Mayer 1574

No. 22: Firm, well-preserved rag paper of the 19th century: Blackwood's Edinburgh Magazine vol. 69 No. 425. New York: Scott 1851

Working with old papers available only in limited quantities has the disadvantage that the supply can run out before all of the relevant measurements have been made. One must simply take this disadvantage into account. One can try to compensate for it by picking out additional papers which come close to the previously used ones on as many variables as possible.

(to page 4)

Table 1

Paper composition

Paper no.	Weight (g/m²)	Fibers (estimated %)				pH[1]			Buffer capacity[2]	Kappa number[3]	Carboxyl groups[4]	Alkali solubility[5]	In percentages						
		Chemical pulp	Hemp, flax, jute	Cotton	Mechanical pulp	Surface	Cold extract	Hot extract					Ash	Magnesium	Calcium	Aluminum	Iron	Sulfate	Silicic acid
1	60	100	0	0	0	7.4	7.8	9.4	35.8 Sr	<5	0.49	15.5	16.1	0.2	10.3	0	0.04	0	1.0
2	80	100	0	0	0	5.5	5.1	5.3	0.5 A	<5	0.33	30.3	15.8	0.1	0.3	3.3	0.05	0.3	7.5
3	80	20	0	0	80	5.7	5.7	5.2	0.25 A	103	0.51	7.3	30.9	0.3	0.2	6.5	0.15	0	14.0
4	80	80	0	20	0	4.7	5.7	5.7	0.65 A	<5	0.18	10.0	0	0	0	0	0	0	0
5	60	0	100	0	0	4.7	4.8	4.8	1.2 A	8.1	0.40	–	0.9	0	0.4	0	0	0.1	0.1
6	60	0	100	0	0	8.1	8.0	8.7	10.45Sr	<5	0.54	–	5.7	0	3.3	0	0.06	0.4	0.7
7	100	40	0	0	60	4.3	4.4	4.5	1.6 A	93.1	0.63	22.8	31.2	0.2	4.2	2.7	0	9.7	6.5
8	70	20	0	0	80	4.4	4.5	4.5	1.6 A	100.5	0.60	22.3	11.9	0.1	0.4	2.0	0.006	0	6.6
9	75	20	0	0	80	5.0	4.8	4.7	1.7 A	105.4	0.55	18.7	12.0	0	0.4	2.7	0.1	0	6.5
11	85	30	10	0	60	4.3	5.8	5.3	0.9 A	65.9	0.50	17.2	30.4	0	0.2	6.2	0	0	18.0
14	80	90	0	10	0	4.2	5.1	5.1	2.3 A	9.8	0.29	46.7	10.9	0	0.6	2.2	0.06	0	5.5
15	55	40	0	0	60	3.5	5.0	4.5	2.1 A	89.7	0.53	19.8	9.6	0	0.4	2.2	0.1	0.3	5.5
16	85	80	20	0	0	3.5	4.6	5.0	1.3 A	21.3	0.79	42.0	23.8	0	0.3	4.5	0.12	0	14.5
18	60	0	100	0	0	7.2	6.2	6.7	0.4 A	<5	0.30	8.4	0.8	0	0.5	0	0	0	0.006
19	150	80	20	0	0	4.5	5.3	5.1	1.6 A	<5	0.35	26.5	27.5	0	0.4	5.4	0.13	0	16.0
20	60	0	100	0	0	5.7	6.0	6.8	0.3 A	<5	0.15	16.7	1.4	0	0.4	0.16	0.02	0	0.4
21	80	0	100	0	0	6.5	6.9	6.9	0.9 Sr	<5	0.23	14.5	1.65	0	0.64	0	0.15	0	0.2
22	60	0	80	20	0	4.8	5.3	5.1	0.1 A	<5	0.08	15.2	0.5	0.07	0.3	0	0	0.1	0.05
Column	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19

1. According to Zellchening specifications V/17/62, resp. DIN 53124.
2. The cold extract from 1 g paper with 50 ml 0.1N HCl is titrated with 0.1N NaOH. This column shows ml below (A) or above (Sr) 50.
3. According to DIN 54357; filler-adjusted.
4. According to Doering: Papier 10 (1956): 140-141; filler-adjusted.
5. According to DIN 54356; filler-adjusted.

ABBEY NEWS 1989 NOVEMBER SUPPL. I P.3

3.2 Artificial aging

The selected papers were subjected to artificial oven aging. As mentioned, the intention was to age them at relatively low temperatures. An arbitrary starting point of 50°C was chosen, and an equally arbitrary rate of increase of 15°C. In determining the level of humidity, we took into account the likelihood of obtaining comparable results most quickly if the amount of moisture present in the paper was held constant at the different aging temperatures.[13] The amount of moisture which paper absorbs at 23°C and 65% RH was selected as the standard. It amounts to approximately 6.5% by weight. The results of a preliminary test for determining this amount of moisture are found in Figures 1-4. The linear regression assumed for the range of observation certainly incorporates an appreciable error, but should be sufficient for present purposes because of the large scatter. This regression yields the following environmental values for the absorption of 6.5% moisture:

50°C and 55-65% RH
65°C and 52-67% RH
80°C and 58-75% RH
95°C and ca. 84% RH (extrapolated)

As a result, for 50°, 65° and 80°, a uniform value for relative humidity of 65% RH (which falls within each of the three ranges) was established. For 95°, the relative humidity was set at 85%. In order to keep conditions reasonably simple, it was necessary to restrict the number of time periods to two. These, however, had to be long enough to produce measurable changes in the test papers at the lower temperatures, as well as at the higher ones. Periods of 305 and 750 hours were established. This resulted in eight different aging conditions:

50°C, 65% RH, 305 hr	80°C, 65% RH, 305 hr
50°C, 65% RH, 750 hr	80°C, 65% RH, 750 hr
65°C, 65% RH, 305 hr	95°C, 85% RH, 305 hr
65°C, 65% RH, 750 hr	95°C, 85% RH, 750 hr

The following variables were measured both before and after aging: tensile strength after folding MD [i.e., after a single folding in a newly developed device], tensile strength after folding CD, pH, kappa number, carboxyl group content, and alkali solubility.

4. Evaluation

4.1 Tensile strength after folding

Tensile strength after specified folding is used, as in the previous study,[6] as an index of usability in libraries and archives.* If one considers the absolute values of these measurements, then Paper No. 14 with 1.38 N MD and 2.44 N CD is the worst of the 18 samples. It would be classified as "endangered."[6] The new papers, Nos. 1-4, are all "strong" to "very strong." Table 2 lists these tensile strength values along with the corresponding rank values. Since the rankings for MD and CD correlate at a confidence level of more than 99.9%, the average value (Table 2, Column 5) was used as a basis for further discussion. Table 7 gives the percentage changes in tensile strength under the various aging conditions for selected papers; Figure 5 shows these values in graphic form for Papers No. 3 and 16. This graph shows, surprisingly, a clear improvement in tensile strength after folding under "mild" aging conditions (50° or 65° at 65% RH); it also shows that the results for MD and CD are substantially analogous. Therefore, only the MD values are given in Figures 6-9 for purposes of simplification, although both MD and CD values have been applied throughout in the statistical analysis. Since these agree in all cases with a high degree of statistical reliability, subsequent calculations were done with the average values of MD + CD (see Table 16).

4.1.1 Aging at 50°C and 65% RH

The values for tensile strength after folding under these aging conditions are given in Table 3, the percentage changes in Table 7 and Figure 6. One can see from the values for this set of conditions an increase in the tensile strength after folding, on the one hand, as great as 264% of the initial value (Paper No. 14 MD after 305 hr aging), and an decrease, on the other hand, to 57% (Paper No. 18 MD after 750 hr). A check of strength values before and after artificial aging shows (Table 16, lines 10 and 11) that the Spearman rank correlation coefficient[16] amounts here to 0.8786 and 0.9080, respectively, and that there is therefore statistical agreement. This means that in spite of some relatively marked variation in individual values, no significant change occurs in the usability rank order as a result of aging at 50°C and 65% RH.

4.1.2 Aging at 65°C and 65% RH

Under these aging conditions, the effects on strength are similar to those obtained at 50°C and 65% RH (Table 4). A maximum increase of 210% in the initial strength (Paper No. 16 after 305 hr) and a decrease of 46% (Paper No. 18 after 750 hr) are recorded. The usability rank order here [Tables 4a and 4b] is also in statistical agreement with the rank order of the initial values [Tables 2a and 2b] (Table 16, rows 12 and 13). Figure 7 shows the relative strengths before and after aging for Papers 16 and 18 together with the strengths for a few papers with more average values.

4.1.3 Aging at 80°C and 65% RH

The increase in measured values of tensile strength after folding observed at 50°C and 65% RH occurs here in only a few cases (Table 5, Figure 8, Papers No. 5 and 21). In most cases, a clear and regular decrease in average measured value is to be observed both after 305 hr and after 750 hr. Figure 8, with its falling curves, resembles the graphs to which one has become accustomed from studies on the artificial aging of paper. Surprisingly, however, the ranking here also remains the same as that of the initial samples (Table 16, lines 14 and 15). The rank order of the papers by usability is not significantly changed by aging at 80°C, either.

4.1.4 Aging at 95°C and 85% RH

The results can be seen in Table 6 and Figure 9. One frequently finds here that the papers have lost all mechanical strength after only 305 hr. After 750 hr, not one

(to page 6)

*Tensile strength (DIN 53 112 T.1), similar to tensile breaking strength according to TAPPI T 404 om-87, was measured with paper specimens of 15 mm width. Only the direct breaking force readings have been documented in newtons (N). The newton is the unit of force required to accelerate a mass of 1 kg to a speed of 1 meter per second in 1 second.

Table 2a

Tensile strength after folding, as a criterion of usability (in newtons, N)

Paper no.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank* N = 18	Rank N = 15	Rank N = 15
1	66.5	2	43.2	1	54.9	1	1	1
2	67.6	1	32.0	2	49.8	2	2	2
3	28.2	7.5	10.8	13	19.5	8	7	6
4	37.3	3.5	25.7	3	31.5	3	3	3
5	5.4	17	3.7	17	4.6	17	–	15
6	33.2	5	16.2	6.5	24.7	5	–	4
7	19.3	9	9.3	13	14.3	12.5	10.5	10.5
8	15.1	13	11.1	11.5	13.1	12.5	10.5	10.5
9	17.1	12	16.3	6.5	16.7	10	8.5	8
11	28.1	7.5	15.8	6.5	22.0	7	6	5
14	1.4	18	2.4	18	1.9	18	15	–
15	6.4	16	7.1	16	6.8	16	14	14
16	11.8	14.5	8.2	14.5	10	14.5	12.5	12.5
18	36.6	3.5	14.6	9	25.6	5	4.5	–
19	30.0	6	20.8	4	25.4	5	4.5	–
20	18.0	10.5	13.6	10	15.8	10	8.5	8
21	11.8	14.5	8.5	14.5	10.2	14.5	12.5	12.5
22	18.3	10.5	15.6	6.5	17	10	–	8
Column	1	2	3	4	5	6	7	8

*In this table rankings are listed for different numbers of N, varying from N=18 to N=6 (columns 6 to 18). These rankings are necessary for the calculation of Spearman rank-order correlation coefficients, as listed in Table 16. For the same reason, these different rankings are also listed in Tables 3 to 15.

Table 2b

Tensile strength after folding, as a criterion of usability (in newtons, N)

Paper no.	Rank N = 14	Rank N = 14	Rank N = 13	Rank N = 13	Rank N = 9	Rank N = 9	Rank N = 8	Rank N = 8	Rank N = 7	Rank N = 6
1	1	1	1	1	1	1	1	1	1	1
2	2	2	2	2	2	2	2	2	2	2
3	5	6	5	5	6	6	6	5	5	5
4	3	3	3	3	3	3	3	3	3	3
5	14	–	13	–	8	8	–	7	–	–
6	–	–	–	–	–	–	–	–	–	–
7	9.5	9.5	9.5	9.5	–	–	–	–	–	–
8	9.5	9.5	9.5	9.5	–	–	–	–	–	–
9	7	7.5	7	7	7	7	7	6	6	6
11	4	5	4	4	5	5	–	4	4	–
14	–	14	–	–	9	9	8	8	7	–
15	13	13	–	13	–	–	–	–	–	–
16	11.5	11.5	11.5	11.5	–	–	–	–	–	–
18	–	–	–	–	4	–	4.5	–	–	–
19	–	4	–	–	–	4	4.5	–	–	4
20	7	7.5	7	7	–	–	–	–	–	–
21	11.5	11.5	11.5	11.5	–	–	–	–	–	–
22	7	–	7	7	–	–	–	–	–	–
Column	9	10	11	12	13	14	15	16	17	18

paper could still be measured, not even the new Papers Nos. 1-4 and the rag paper, No. 18. The series of samples was abbreviated due to lack of material.

4.2 pH

Initial pH values were measured by methods conventionally employed in the paper industry (surface pH, pH cold extraction, and pH hot extraction). The rank-order values shown in Table 9 have a very close correlation (over 99%) with usability (Table 16, line 50). Since the surface pH is the simplest and fastest to determine, only this value was used in subsequent investigations. Figure 10 shows the relationship between tensile strength after folding and surface pH. The regression curves show a positive slope whether or not the new papers are taken into consideration. In generalizing the values found for the samples examined, one can conclude that the higher the pH of paper, the greater its usability. This would be a statistically significant formulation of the generally accepted relationship of paper quality and pH, for the pH range involved here (3.5 to 8.1).

After artificial aging, however, the pH values behave differently. Low initial values seem to increase with aging; high ones seem more likely to decrease. The pH range of 3.5-8.1 is narrowed by artificial aging at 80°C and 65% RH to a range of 4.0-6.8. If one considers the individual stages of aging, no uniform picture can be seen (Table 19). A correlation between pH and usability exists only for the aging conditions of 50°C, 65% RH, 305 hr and 80°C, 65% RH, 750 hr.

4.3 Cellulose chemistry variables

This study was undertaken despite many misgivings concerning the determination of such characteristics as alkali solubility, carboxyl group content and kappa number of papers. The values found before and after aging as well as their ranking are found in Tables 10-15. Values for these chemical characteristics after aging under the various conditions also show a good correlation with the initial values, with the exception of aging at 95°C (Table 17); here, agreement is found only with surface pH and kappa number. From this, one can conclude that chemical change is approximately identical in tendency in all of the papers at all temperatures up through 80°C.

However, a comparison of the pre- and post-aging values for the chemical characteristics with initial usability (Table 18) reveals partial agreement between usability and these same two variables, surface pH and kappa number.

A good correlation was found between alkali solubility and usability only after artificial aging of the papers at 80°C and 65% RH. For carboxyl groups, a correlation with usability existed only after aging at 95°C, 85% RH, 305 hr. Kappa numbers show precisely the reverse: no correlation with usability after aging at 80°C, but a definite correlation under all the other conditions.

5. Details

In the above, many surprising and contradictory results are reported. The same is also found during an examination of the details.

5.1 Strength loss

Only by artificial aging at 95°C and 85% RH (305 hr) was it possible to reduce new papers Nos. 1-4 to a state of usability resembling that of the poor papers Nos. 14 and 15. Following this artificial aging, all of the papers except No. 21 CD lost 70-100% of their strength, even Paper No. 18, which had not only proven its resistance to aging by enduring 127 years of storage at room temperature without problems, but which might have been expected, on the basis of comparison to much older papers with a similar composition, to last even longer.

The longer aging period at 95°C makes this paper, like all the others (including Paper No. 21) completely unusable. It puts all paper in a condition which has never been observed as a result of natural aging. The samples were in such a weak, almost carbonized state that they resembled fire-damaged material (Figure 11).

5.2 Groundwood content

The percentage of strength loss resulting from 305 hours at 95°C is (again with the exception of Paper No. 21) lowest with the 80%-groundwood, acidic papers No. 3 and 9. This is in contradiction to the general observation encountered in archives and libraries, that groundwood-content paper loses more strength than groundwood-free paper during natural aging.

5.3 Increase in strength

All of the papers lost strength at 95°C, the highest stress to which the papers were subjected. At lower stress levels (50°C and 65°C), they gained strength in some cases. Papers already naturally aged showed a greater and more frequent improvement. All variations occur: continuous increase with both shorter and longer aging period; an initial increase followed by a decrease and vice versa; and a continuous decrease. Even if the chemical processes of natural aging in new papers take place first, during the unknown number of years equivalent to 305 or 750 hours of artificial aging at 50°C or 65°C, in a sequence and with a pattern of interaction that actually improves usability before the paper passes on to the deterioration which experience tells us is inevitable, this is improbable with already aged papers. With Papers No. 15, 16 and 21, for example, one can postulate without reservation that since their manufacture 43, 75 and 407 years ago, respectively, a strength loss has occurred which has brought them to Class IV, "usable" [out of a total of seven classes, the last of which is "unusable"].[6] Suppose that they had been stored under natural conditions over an unknown number of years corresponding to 305 or 750 hours of artificial aging under the conditions selected here: it is hardly conceivable that they could have gained back their strength, solely through this additional storage, to such a degree that they could again be "usable without limitation" or "strong."

6. Results

6.1 Validity of artificial aging

The technique of artificial aging is based on the assumption of parallelism. "Aging" is the sum of overlapping and mutually influencing chemical processes; it is assumed that they take place, at higher temperatures to

(to page 15)

Table 3a

Aging at 50°C and 65° RH, 305 hours: Tensile strength after folding (N)

Paper No.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank N = 15	Rank N = 14
1	66.9	1	29.2	1	48.1	1	1
2	56.7	2	26.5	2	41.6	2	2
3	28.5	4.5	11.2	10	19.9	6	6
4	32.2	3	20.2	3	26.2	3	3
5	–	–	–	–	–	–	–
6	–	–	–	–	–	–	–
7	16.9	10	9.7	13.5	13.3	10.5	9.5
8	14.7	12	10.9	12	12.8	12.5	11.5
9	15.0	12	12.1	10	13.6	10.5	9.5
11	28.7	4.5	16.4	6	22.5	4	4
14	3.7	15	2.0	15	2.8	15	14
15	14.2	12	9.0	13.5	11.6	14	13
16	19.6	8.5	11.1	10	15.3	9	8
18	22.1	6.5	16	6	19.1	7	–
19	22.8	6.5	18.3	4	20.5	5	5
20	12.8	14	12.8	8	12.8	12.5	11.5
21	19.3	8.5	15.9	6	17.6	8	7
22	–	–	–	–	–	–	–
Column	1	2	3	4	5	6	7

Table 3b

Aging at 50°C and 65° RH, 750 hours: Tensile strength after folding (N)

Paper No.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank N = 15	Rank N = 14
1	70.6	1	30	1	50.1	1	1
2	59.8	2	26.2	2	43.1	2	2
3	31.3	4.5	10.9	11.5	21.2	6	6
4	34.4	3	20.7	4	27.6	3	3
5	–	–	–	–	–	–	–
6	–	–	–	–	–	–	–
7	20.1	8.5	10.1	13	15.1	10.5	9.5
8	15.8	12	10.8	11.5	13.3	12	11
9	17.7	10.5	14	9.5	15.8	10.5	9.5
11	31.4	4.5	15.9	5.5	23.6	5	5
14	3.6	15	2.8	14	3.2	15	14
15	12.5	13.5	6.3	15	9.4	14	13
16	23.9	7	14.1	9.5	19	7	7
18	21	8.5	15.3	5.5	18.1	8	–
19	28.3	6	25.6	3	26.9	4	4
20	18	10.5	16.5	7.5	17.2	9	8
21	13.2	13.5	12.1	7.5	12.6	13	12
22	–	–	–	–	–	–	–
Column	9	10	11	12	13	14	15

Table 4a

Aging at 65%C and 65% RH, 305 hours: Tensile strength after folding (N)

Paper No.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank N = 15
1	65.6	1	28.6	1	47.1	1
2	58.3	2	26.3	2.5	42.3	2
3	28.1	4	11.0	9	19.6	6
4	30.8	3	20.6	4	25.7	4
5	–	–	–	–	–	–
6	–	–	–	–	–	–
7	18.8	8.5	8.6	12	13.7	10
8	11.0	13	8.3	12	9.6	13.5
9	14.3	11	9.3	10	11.8	11
11	24.5	6.5	13.5	7.5	19.0	6
14	2.7	15	2.1	15	2.4	15
15	10.9	13	7.1	14	9.0	13.5
16	24.8	6.5	15.0	5.5	19.9	6
18	18.7	8.5	15.2	5.5	17.0	8
19	26.3	5	26.9	2.5	26.6	3
20	17.1	10	13.3	7.5	15.2	9
21	11.8	13	8.5	12	10.1	12
22	–	–	–	–	–	–
Column	1	2	3	4	5	6

Table 4b

Aging at 65°C and 65% RH, 750 hours: Tensile strength after folding (N)

Paper No.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank N = 15
1	66.4	1	33.3	1	49.9	1
2	56.3	2	26.7	2	41.5	2
3	27.3	4.5	9.8	12	18.6	7
4	32.1	3	20.0	4	26.0	3
5	–	–	–	–	–	–
6	–	–	–	–	–	–
7	18.7	9.5	12.7	9	15.7	9.5
8	11.8	13	8.1	13	9.9	13
9	16.5	12	10.1	10.5	13.3	12
11	23.0	7	14.5	6	18.7	7
14	2.3	15	2.8	15	2.5	15
15	8.9	14	6.5	14	7.7	14
16	21.4	8	13.8	8	17.6	7
18	17.0	11	15.0	6	16.0	9.5
19	26.4	4.5	21.2	3	23.8	4
20	25.4	6	15.3	6	20.3	5
21	18.3	9.5	11.1	10.5	14.7	11
22	–	–	–	–	–	–
Column	9	10	11	12	13	14

Table 5a

Aging at 80°C and 65° RH, 305 hours: Tensile strength after folding (N)

Paper No.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank N = 15	Rank N = 14	Rank N = 13	Rank N = 13
1	62.2	1	37.7	1	50.0	1	1	1	1
2	54.3	2	27.4	2	40.8	2	2	2	2
3	24.1	4.5	9.6	8.5	16.9	5.5	4.5	4.5	4.5
4	29.6	3	19.5	3	24.6	3	3	3	3
5	7.3	13	4.7	13	6.0	13.5	12.5	12.5	–
6	23.7	4.5	17.9	4	20.8	4	–	–	–
7	16.6	7.5	7.5	10.5	12.0	9	8	8	8
8	12.9	10.5	7.0	10.5	9.9	11	10	10	10
9	14.3	9	8.9	8.5	11.6	9	8	8	8
11	21.3	6	14.0	6	17.6	5.5	4.5	4.5	4.5
14	–	–	–	–	–	–	–	–	–
15	4.2	15	4.0	15	4.1	15	14	–	13
16	9.0	12	5.3	13	7.1	12	11	11	11
18	–	–	–	–	–	–	–	–	–
19	–	–	–	–	–	–	–	–	–
20	6.9	14	5.0	13	5.9	13.5	12.5	12.5	12
21	13.3	10.5	11.3	7	12.3	9	8	8	8
22	16.5	7.5	15.5	5	16.0	7	6	6	6
Column	1	2	3	4	5	6	7	8	9

Table 5b

Aging at 80°C and 65° RH, 750 hours: Tensile strength after folding (N)

Paper No.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank N = 14	Rank N = 13	Rank N = 13
1	65.7	1	28.9	1	47.3	1	1	1
2	39.5	2	24.3	2	31.9	2	2	2
3	18.4	4	7.2	8	12.8	6	6	6
4	20.6	3	15.9	3	18.3	3	3	3
5	6.8	11	4.3	11.5	5.6	11	11	–
6	–	–	–	–	–	–	–	–
7	5.0	12	3.9	11.5	4.5	12	12	11
8	12.0	8	8.0	8	10.0	8	8	8
9	8.9	9.5	6.6	10	7.8	9.5	9.5	9.5
11	15.8	6	9.5	6	12.6	6	6	6
14	–	–	–	–	–	–	–	–
15	2.0	14	1.4	14	1.7	14	–	13
16	3.2	13	2.7	13	2.9	13	13	12
18	–	–	–	–	–	–	–	–
19	–	–	–	–	–	–	–	–
20	17.3	5	13.8	4.5	15.6	4	4	4
21	8.7	9.5	7.8	8	8.2	9.5	9.5	9.5
22	14.0	7	12.9	4.5	13.5	6	6	6
Column	10	11	12	13	14	15	16	17

Table 6a

Aging at 95°C and 85% RH, 305 hours: Tensile strength after folding (N)

Paper No.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank N = 9	Rank N = 7	Rank N = 7
1	9	7.5	2.8	6	1.4	6	6	5
2	12.1	1	7.9	1	10.0	1	1	1
3	6.9	2.5	3.5	4.5	5.2	3	3	3
4	7.1	2.5	5.3	2.5	6.2	2	2	2
5	0	7.5	0	8	0	8	–	–
6	–	–	8.7	–	–	–	–	–
7	–	–	–	–	–	–	–	–
8	–	–	–	–	–	–	–	–
9	5.2	4	3.1	4.5	4.2	4.5	4.5	4
11	0	7.5	0	8	0	8	–	6.5
14	0	7.5	0	8	0	8	7	6.5
15	–	–	–	–	–	–	–	–
16	–	–	–	–	–	–	–	–
18	4.0	5	4.5	2.5	4.2	4.5	4.5	–
19	–	–	0	–	–	–	–	–
20	–	–	–	–	–	–	–	–
21	–	–	8.6	–	–	–	–	–
22	–	–	–	–	–	–	–	–
Column	1	2	3	4	5	6	7	8

Table 6b

Aging at 95°C and 85% RH, 750 hours: Tensile strength after folding (N)

Paper No.	MD	Rank	CD	Rank	$\frac{MD + CD}{2}$	Rank N = 9	Rank N = 8	Rank N = 7	Rank N = 6
1	0	5	0	5.5	0	5.5	5	4.5	4
2	0	5	0	5.5	0	5.5	5	4.5	4
3	0	5	0	5.5	0	5.5	5	4.5	4
4	0	5	0	5.5	0	5.5	5	4.5	4
5	0	5	0	5.5	0	5.5	5	–	–
6	–	–	–	–	–	–	–	–	–
7	–	–	–	–	–	–	–	–	–
8	–	–	–	–	–	–	–	–	–
9	0	5	0.9	1	0.5	3	1	1	1
11	0	5	0	5.5	0	5.5	5	4.5	–
14	0	5	0	5.5	0	5.5	5	4.5	–
15	–	–	–	–	–	–	–	–	–
16	–	–	–	–	–	–	–	–	–
18	0	5	0	5.5	0	5.5	–	–	4
19	–	–	0	–	–	–	–	–	–
20	–	–	–	–	–	–	–	–	–
21	–	–	0	–	–	–	–	–	–
22	–	–	–	–	–	–	–	–	–
Column	9	10	11	12	13	14	15	16	17

Table 7

Change in tensile strength after folding (average value), as a percentage of the original value

Paper No.	$\frac{MD + CD}{2}$	%	50°C 65% RH		65°C 65% RH		80°C 65% RH		95°C 85% RH	
			305 h	750 h	305 h	750 h	305 h	750 h	305 h	750 h
1	54.9	100	87.7	91.3	85.9	90.8	91.0	86.2	2.6	0
2	49.8	100	83.6	86.5	85.9	83.3	82.0	64.0	20.1	0
3	19.5	100	101.8	108.6	100.4	95.3	86.6	65.6	26.8	0
4	31.5	100	82.3	86.6	80.7	81.7	77.3	37.5	19.6	0
5	4.5	100	–	–	–	–	132.5	200.1	0	0
6	24.7	100	–	–	–	–	48.6	–	–	–
7	14.3	100	92.9	106.0	95.7	109.9	84.0	31.5	–	–
8	13.1	100	97.8	101.7	73.5	75.5	75.5	76.4	–	–
9	16.6	100	81.9	95.5	71.4	80.4	70.1	47.1	25.4	2.6
11	22.0	100	102.5	107.5	86.5	85.0	80.0	57.3	0	0
14	1.9	100	147.1	167.5	125.1	130.9	–	–	0	0
15	6.8	100	172.0	139.2	132.5	113.9	60.7	23.2	–	–
16	10.0	100	153.1	189.9	198.6	175.8	70.9	29.0	–	–
18	25.6	100	74.4	70.8	66.2	62.5	–	–	16.6	0
19	25.4	100	80.7	105.9	104.6	95.6	–	–	–	–
20	15.8	100	81.0	109.0	96.4	128.5	37.3	98.7	–	–
21	10.1	100	174.2	124.8	100.1	145.3	121.3	85.0	–	–
22	17.0	100	–	–	–	–	94.3	29.6	–	–
Column	1	2	3	4	5	6	7	8	9	10

Table 8

Surface pH

Paper No.	Measured value	Rank N = 18	Rank N = 15	Rank N = 15	Rank N = 14	Rank N = 7
1	7.4	2	1	2	1	1
2	5.5	7	6	6	5	3
3	5.7	5.5	4.5	4.5	3.5	2
4	4.7	10.5	8	9.5	8.5	5
5	4.7	10.5	–	9.5	8.5	–
6	8.1	1	–	1	–	–
7	4.5	14.5	11.5	12.5	11.5	–
8	4.4	15	10	11	10	–
9	5.0	8	7	7	6	4
11	4.5	14.5	11.5	12.5	11.5	6
14	4.2	16	13	–	–	7
15	3.5	17.5	14.5	14.5	13.5	–
16	3.5	17.5	14.5	14.5	13.5	–
18	7.2	3	2	–	–	–
19	4.5	12	9	–	–	–
20	5.7	5.5	4.5	4.5	3.5	–
21	6.5	4	3	3	2	–
22	4.8	9	–	8	7	–
Column	1	2	3	4	5	6

Table 9

Surface pH after aging

Paper No.	50°C and 65% RH 305 h		50°C and 65% RH 750 h		65°C and 65% RH 305 h		65°C and 65% RH 750 h		80°C and 65% RH 305 h		80°C and 65% RH 750 h		95°C and 85% RH 305 h		95°C and 85% RH 750 h	
	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank
1	8.5	1	8.7	1	7.3	1	7.2	1	7.1	2	6.8	1	7.3	1	7.1	1
2	5.1	6.5	5.3	8.5	5.5	4	5.0	10	4.5	8.5	4.8	6	5.2	4	5.6	2
3	5.5	4	5.5	6.5	4.6	13.5	4.5	12	4.3	11.5	5.0	5	5.4	2	5.5	3
4	4.8	11.5	5.1	11.5	5.3	6.5	5.7	2	5.4	3	4.6	7	4.8	5	4.8	6
5	–	–	–	–	–	–	–	–	4.3	11.5	4.3	9	–	–	–	–
6	–	–	–	–	–	–	–	–	7.9	1	–	–	–	–	–	–
7	4.6	13.5	4.9	14	4.6	13.5	5.1	8.5	4.0	14.5	4.1	11	–	–	–	–
8	4.8	11.5	5.1	11.5	5.0	9	5.2	6.5	4.5	8.5	4.0	13.5	–	–	–	–
9	5.0	9	5.3	8.5	4.9	10.5	5.1	8.5	4.1	13	4.1	11	5.3	3	5.4	4
11	5.0	9	5.6	4	4.7	13.5	4.4	13	4.5	8.5	4.5	8	4.4	6	4.6	7
14	4.6	13.5	5.2	10	4.9	10.5	4.8	11	–	–	–	–	4.1	7	5.0	5
15	4.5	15	5.0	13	5.2	8	4.1	15	4.0	14.5	4.0	13.5	–	–	–	–
16	5.0	9	4.7	15	4.6	13.5	4.3	14	4.5	8.5	4.1	11	–	–	–	–
18	5.6	3	5.6	4	5.3	6.5	5.3	5	–	–	–	–	–	–	–	–
19	5.3	5	5.6	4	5.4	5	5.2	6.5	–	–	–	–	–	–	–	–
20	5.1	6.5	5.5	6.5	5.7	3	5.4	4	5.1	5	5.3	3	–	–	–	–
21	6.0	2	6.1	2	5.8	2	5.6	3	5.3	4	6.6	2	–	–	–	–
22	–	–	–	–	–	–	–	–	5.0	6	5.2	4	–	–	–	–
Column	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

Table 10

Carboxyl group content

Paper No.	Measured value	Rank N = 18	Rank N = 15	Rank N = 14	Rank N = 13	Rank N = 9
1	0.49	10	8	7	7	6
2	0.33	7	6	5	5	4
3	0.51	12	10	9	9	8
4	0.18	3	2	2	3	1
5	0.40	9	–	–	6	5
6	0.54	14	–	–		
7	0.63	17	14	13	12	
8	0.60	16	13	12	11	
9	0.55	15	12	11	10	9
11	0.50	11	9	8	8	7
14	0.29	5	4	4	–	2
15	0.53	13	11	10	–	
16	0.79	18	15	14	13	
18	0.30	6	5	–	–	3
19	0.35	8	7	6	–	
20	0.15	2	1	1	2	
21	0.23	4	3	3	4	
22	0.08	1	–	–	1	
Column	1	2	3	4	5	6

Table 11

Carboxyl group content after aging

	50°C and 65% RH				65°C and 65% RH				80°C and 65% RH				95°C and 85% RH			
	305 h		750 h		305 h		750 h		305 h		750 h		305 h		750 h	
Paper No.	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank
1	0.32	8	0.17	8	0.31	8	0.22	9	0.19	7	0.17	7	0.54	6.5	0.49	6
2	0.17	4	0.10	3	0.16	5	0.15	6.5	0.12	4.5	0.11	3	0.18	3	0.55	7
3	0.44	11	0.20	9	0.41	11	0.30	10	0.34	12.5	0.34	13	0.42	4	0.31	2.5
4	0.10	1	0	1	0.06	1	0.05	3	0.03	1	0	1	0.07	1	0	1
5	–	–	–	–	–	–	–	–	0.15	6	0.14	5	0.56	8	0.47	5
6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7	0.60	14	0.46	14	0.36	10	0.38	13	0.34	12.5	0.33	12	–	–	–	–
8	0.50	13	0.45	13	0.51	15	0.41	14	0.22	9	0.26	9	–	–	–	–
9	0.48	12	0.31	11	0.43	12	0.35	12	0.26	11	0.30	11	0.45	5	0.35	4
11	0.22	6	0.22	10	0.48	13	0.34	11	0.25	10	0.28	10	0.54	6.5	0.90	8
14	0.26	7	0.16	6.5	0.26	7	0.15	6.5	–	–	–	–	0.75	9	1.58	9
15	0.42	10	0.41	12	0.49	14	0.44	15	–	–	–	–	–	–	–	–
16	0.40	9	0.11	4	0.32	9	0.19	8	0.21	8	0.25	8	–	–	–	–
18	–	–	–	–	0.11	3	0.02	1	–	–	–	–	0.14	2	0.31	2.5
19	0.21	5	0.16	6.5	0.21	6	0.03	2	–	–	–	–	0.16	–	0.37	–
20	0.11	2	0.09	2	0.11	3	0.10	4	0.11	3	0.14	5	–	–	–	–
21	0.12	3	0.13	5	0.11	3	0.13	5	0.12	4.5	0.14	5	–	–	–	–
22	–	–	–	–	–	–	–	–	0.07	2	0.07	2	–	–	–	–
Column	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

Table 12

Kappa number

Paper No.	Measured value	Rank N = 16	Rank N = 15	Rank N = 14	Rank N = 9	Rank N = 8
1	<5	5	4	3.5	2.5	2
2	<5	5	4	3.5	2.5	2
3	103	17	14	13	8	7
4	<5	5	4	3.5	2.5	2
5	8.1	10	–	7	5	4
6	<5	5	–	–	–	–
7	93.1	15	12	11	–	–
8	100.5	16	13	12	–	–
9	105.4	18	15	14	9	8
11	65.9	13	10	9	7	6
14	9.8	11	8	–	6	5
15	89.7	14	11	10	–	–
16	21.3	12	9	8	–	–
18	<5	5	4	–	2.5	–
19	<5	5	4	–	–	–
20	<5	5	4	3.5	–	–
21	<5	5	4	3.5	–	–
22	<5	5	–	3.5	–	–
Column		1	2	3	4	5	6

Table 13

Kappa numbers after aging

	50°C and 65% RH				65°C and 65% RH				80°C and 65% RH				95°C and 85% RH			
	305 h		750 h		305 h		750 h		305 h		750 h		305 h		750 h	
Paper No.	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank	Measured value	Rank
1	<5	3.5	<5	3.5	<5	4	<5	3.5	<5	2.5	<5	2.5	19.5	4	33.6	4
2	<5	3.5	<5	3.5	<5	4	<5	3.5	<5	2.5	<5	2.5	<5	2	8.1	2
3	97	12	99	13	105	13	107	13.5	103	12	103	12.5	110	8	117	8
4	<5	3.5	<5	3.5	<5	4	<5	3.5	<5	2.5	<5	2.5	<5	2	<5	1
5	–	–	–	–	–	–	–	–	8.1	6.5	8.6	6.5	25.8	5.5	25.4	3
6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7	92.0	11	91.8	11	91.8	11	102.4	12	92.1	10	92.6	10	–	–	–	–
8	105.9	14	105.8	14	106.4	14	108.8	15	109.9	14	95.5	11	–	–	–	–
9	107.9	15	110.8	15	109.4	15	106.7	13.5	107.1	13	107.8	14	112.9	9	112.9	7
11	67.3	10	67.3	10	68.2	10	68.5	10	69.1	9	70.5	9	76.1	7	89.1	6
14	9.8	8	9.8	8	9.7	8	10.8	8	–	–	–	–	35.5	5.5	61.2	5
15	99.1	13	94.4	12	97.9	12	97.4	11	95.8	11	103.3	12.5	–	–	–	–
16	21.3	9	21.3	9	14.6	9	15.4	9	22.3	8	24.4	8	–	–	–	–
18	<5	3.5	<5	3.5	<5	4	<5	3.5	–	–	–	–	<5	2	12.9	–
19	<5	3.5	<5	3.5	<5	4	<5	3.5	–	–	–	–	12.1	–	20.3	–
20	<5	3.5	<5	3.5	<5	4	<5	3.5	8.4	6.5	9.0	6.5	–	–	–	–
21	6.7	7	5.5	7	<5	4	7.8	7	6.5	5	7.8	5	–	–	–	–
22	–	–	–	–	–	–	–	–	5	2.5	<5	2.5	–	–	–	–
Column	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

Table 14

Alkali solubility

Paper No.	Measured value	Rank N = 15	Rank N = 13	Rank N = 7	Rank N = 5
1	13.5	5	4.5	4	3
2	20.3	10	10	6	5
3	7.3	1	1	1	1
4	10.0	3	2	3	2
5	–	–	–	–	–
6	–	–	–	–	–
7	22.8	11.5	11.5	–	–
8	22.3	11.5	11.5	–	–
9	18.7	8	8	5	4
11	17.2	7	7	–	–
14	46.7	15	–	7	–
15	19.8	9	9	–	–
16	42.0	14	13	–	–
18	8.4	2	–	2	–
19	26.5	13	–	–	–
20	16.7	6	6	–	–
21	14.0	4	3	–	–
22	15.2	–	4.5	–	–
Column	1	2	3	4	5

Table 15

Alkali solubility after aging

Paper No.	50°C and 54% RH 305 h Measured value	Rank	50°C and 54% RH 750 h Measured value	Rank	65°C and 65% RH 305 h Measured value	Rank	65°C and 65% RH 750 h Measured value	Rank	80°C and 65% RH 305 h Measured value	Rank	80°C and 65% RH 750 h Measured value	Rank	95°C and 85% RH 305 h Measured value	Rank	95°C and 85% RH 750 h Measured value	Rank
1	18.2	6	17.4	6	19.0	7	18.2	5.5	20.0	5	21.7	5	50.9	5	65.7	5
2	19.8	10	19.1	8	20.9	8	19.3	7	19.6	4	20.3	4	52.0	3	56.1	4
3	10.1	1	9.5	1	10.5	1	11.1	1	11.4	1	12.3	2	20.7	1	28.5	1
4	11.4	2	11.9	2	12.0	2	12.9	2	12.4	2	12.6	1	35.4	4	45.6	3
5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7	26.5	12	24.6	11	23.6	11	22.0	9	32.0	12	36.9	12	–	–	–	–
8	19.6	9	22.9	9	21.6	9.5	23.4	11.5	28.7	11	35.0	11	–	–	–	–
9	18.6	7	18.6	7	18.6	6	20.0	8	23.0	8	24.0	6	26.3	2	30.5	2
11	23.2	11	25.6	12	25.3	12	23.2	11.5	24.0	9	30.7	10	–	–	–	–
14	48.8	15	55.1	15	55.1	15	59.7	15	–	–	–	–	92.1	8	–	–
15	19.1	8	23.6	10	21.9	9.5	22.9	10	26.6	10	29.8	9	–	–	–	–
16	39.5	14	42.5	14	36.7	14	42.6	14	43.7	13	49.7	13	–	–	–	–
18	15.5	4	15.2	3	16.4	3.5	16.5	3	–	–	–	–	53.2	6	–	–
19	30.1	13	30.0	13	27.8	13	33.8	13	–	–	–	–	73.6	7	81.4	4
20	16.7	5	16.8	5	16.6	3.5	17.2	4	17.8	3	19.0	3	–	–	–	–
21	14.1	3	15.6	4	17.2	5	18.2	5.5	20.8	6	27.3	8	–	–	–	–
22	–	–	–	–	–	–	–	–	21.2	7	25.0	7	–	–	–	–
Column	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16

Results (from page 6)

which they are exposed over a longer period of time, in a uniformly intensified and accelerated fashion, and that these processes reveal themselves through uniform changes in measurements on the aged material. The studies reported here have shown that such uniformities do not exist. This becomes especially clear when one considers the changes caused by parallel changes in the test conditions, namely, temperature increases of 15°, from 50° to 65°, from 65° to 80°, and from 80° to 95° with the same time period or the longer one (750 instead of 305 hours) under otherwise identical conditions. The values found give the impression that the sequence and interaction of the processes that constitute aging differ in a temperature-specific way. They are, at 50°C, completely different than those at 65°, 80° and 95°. Only by a parallel coincidence, that is, if values at one temperature equalled those at another, could the different intensities of the processes be seen as evidence for their acceleration.

6.2 How should artificial aging be done?

There is no possibility that the sum, sequence, mutual influence of the [chemical and physical] processes of aging could be the same at higher temperatures (at least not at 50°, 65° or 95°) as they are at room temperature, differing only in degree. If they are the same at all, it is most likely under the aging conditions of 80°C and 65% RH. Figure 8 and Tables 17-19 review the statistical relationships found. In any case, artificial aging at 80°C and 65% RH leads to practical, useful values. That is its advantage. In evaluating its results--as well as the results of other aging methods conventionally used elsewhere and likewise leading to practical, useful values--one must, however, be aware of its described character. Perhaps one should go so far as to include dry oven aging (which was not examined in detail here) in this type of testing. The conditions of dry oven aging, of course, are very far removed from the conditions of natural aging, and the probability of the above-mentioned consistency occurring with dry oven aging would therefore be especially slight.

[Editor's postscript: Since the first appearance of this article in the German language in Restaurator, the recommended conditions have been incorporated into an international standard, ISO/DIS 5630/3-1986, "Paper and Board - Accelerated Ageing - Part 3, Moist heat treatment at 80°C and 65% Relative Humidity."]

Table 16

Spearman rank-order correlation coefficients (r_S) for paired rankings of individual papers (I and II), with size of random sample N, test value P, and resulting level of confidence S

	Line	I		II		N	r_S §	P *	S (1-α)
		Table	Column	Table	Column				
Column (this table)	1	2	3	4	5	6	7	8	9
	1	2	2	2	4	18	0.8865	16.56	>99.9
	2	3a	2	3a	4	15	0.5357	2.71	>95.0
	3	3b	10	3b	12	15	0.7321	5.69	>99.9
	4	4a	2	4a	4	15	0.8821	14.34	>99.9
	5	4b	10	4b	12	15	0.8411	10.36	>99.9
	6	5a	2	5a	4	15	0.9179	21.01	>99.9
	7	5b	10	5b	12	14	0.9440	30.01	>99.9
	8	6a	2	6a	4	9	0.9208	16.02	>99.9
	9	6b	10	6b	12	9	0.8500	8.10	>99.9
	10	2	7	3a	6	15	0.8786	13.89	>99.9
	11	2	7	3b	14	15	0.9080	18.66	>99.9
	12	2	7	4a	6	15	0.8696	12.87	>99.9
	13	2	7	4b	14	15	0.8384	10.17	>99.9
	14	2	8	5a	6	15	0.9089	18.85	>99.9
	15	2	9	5b	14	14	0.8484	10.48	>99.9
	16	2	13	6a	6	9	0.5625	2.18	<95.0
	17	2	13	6b	14	9	0.2000	0.55	<95.0
	18	8	3	9	2	15	0.8518	11.19	>99.9
	19	8	3	9	4	15	0.7571	6.40	>99.9
	20	8	3	9	6	15	0.6473	4.02	>99.0
	21	8	3	9	8	15	0.7250	5.51	>99.9
	22	8	4	9	10	15	0.6339	3.82	>99.0
	23	8	5	9	12	14	0.8440	10.16	>99.9
	24	8	6	9	14	7	0.9643	2.00	>99.0
	25	8	6	9	16	7	0.8571	8.00	>95.0
	26	10	4	11	2	14	0.8901	14.85	>99.9
	27	10	4	11	4	14	0.7198	5.17	>99.9
	28	10	3	11	6	15	0.8179	8.91	>99.9
	29	10	3	11	8	15	0.7616	6.54	>99.9
	30	10	5	11	10	13	0.8514	10.49	>99.9
	31	10	5	11	12	13	0.8077	7.71	>99.9
	32	10	6	11	14	9	0.2208	0.61	<95.0
	33	10	6	11	16	9	-0.4708	1.60	<95.0
	34	12	3	13	2	15	0.9634	48.33	>99.9
	35	12	3	13	4	15	0.9741	68.71	>99.9
	36	12	3	13	6	15	0.9929	251.48	>99.9
	37	12	3	13	8	15	0.9696	58.47	>99.9
	38	12	4	13	10	14	0.9484	32.65	>99.9
	39	12	4	13	12	14	0.9473	31.95	>99.9
	40	12	5	13	14	9	0.9708	44.68	>99.9
	41	12	6	13	16	8	0.9048	8.00	>99.0
	42	14	2	15	2	15	0.9420	30.13	>99.9
	43	14	2	15	4	15	0.9259	23.39	>99.9
	44	14	2	15	6	15	0.9071	18.47	>99.9
	45	14	2	15	8	15	0.9196	21.50	>99.9
	46	14	3	15	10	13	0.8187	8.23	>99.9
	47	14	3	15	12	13	0.7473	5.61	>99.9
	48	14	4	15	14	7	0.3571	36.00	<95.0
	49	14	5	15	16	5	0.5000	10.00	<95.0
	50	2	6	8	2	18	0.5739	5.45	>99.0
	51	2	7	9	2	15	0.5031	2.43	>95.0
	52	2	7	9	4	15	0.5018	2.42	>95.0
	53	2	7	9	6	15	0.4071	1.76	<95.0
	54	2	7	9	8	15	0.4768	2.22	>95.0
	55	2	8	9	10	15	0.5473	2.82	>95.0

	Line	I		II		N	r_S	P	S ($1-\alpha$)
		Table	Column	Table	Column				
Column	1	2	3	4	5	6	7	8	9
	56	2	8	9	12	15	0.5099	2.39	>95.0
	57	2	17	9	14	7	0.4643	30.00	<95.0
	58	2	17	9	16	7	0.4643	30.00	<95.0
	59	2	6	10	2	18	0.1785	0.74	<95.0
	60	2	10	11	2	14	0.3330	1.30	<95.0
	61	2	10	11	4	14	0.2857	1.08	<95.0
	62	2	7	11	6	15	0.3554	1.47	<95.0
	63	2	7	11	8	15	0.3973	1.70	<95.0
	64	2	11	11	10	13	0.1346	0.45	<95.0
	65	2	11	11	12	13	0.1456	0.49	<95.0
	66	2	13	11	14	9	0.5875	2.37	=95.0
	67	2	13	11	16	9	0.2042	0.56	<95.0
	68	2	6	12	2	18	0.5387	3.04	>99.0
	69	2	7	13	2	15	0.6000	3.38	>99.0
	70	2	7	13	4	15	0.5750	3.10	>99.0
	71	2	7	13	6	15	0.5018	2.42	>95.0
	72	2	7	13	8	15	0.5679	3.02	>99.0
	73	2	9	13	10	14	0.4099	1.71	<95.0
	74	2	9	13	12	14	0.4132	1.73	<95.0
	75	2	13	13	14	9	0.6292	2.76	>95.0
	76	2	16	13	16	8	0.3810	52.00	<95.0
	77	2	7	14	2	15	0.4580	2.09	<95.0
	78	2	7	15	2	15	0.3375	1.37	<95.0
	79	2	7	15	4	15	0.0339	0.12	<95.0
	80	2	7	15	6	15	0.4116	1.79	<95.0
	81	2	7	15	8	15	0.1013	0.37	<95.0
	82	2	12	15	10	13	0.6456	3.67	>99.0
	83	2	12	15	12	13	0.6566	3.83	>99.0
	84	2	15	15	14	8	0.0893	76.50	<95.0
	85	2	18	15	16	6	-0.6000	56.00	<95.0
	86	3a	6	9	2	15	0.5982	3.36	>99.0
	87	3a	7	11	2	14	0.3846	1.56	<95.0
	88	3a	6	13	2	15	0.5536	2.88	>95.0
	89	3a	6	15	2	15	0.2750	1.07	<95.0
	90	3b	14	9	4	15	0.3473	1.42	<95.0
	91	3b	15	11	4	14	0.4022	1.66	<95.0
	92	3b	14	13	4	15	0.5518	2.86	>95.0
	93	3b	14	15	4	15	0.2402	0.92	<95.0
	94	4a	6	9	6	15	0.2777	1.08	<95.0
	95	4a	6	11	6	15	0.3420	1.40	<95.0
	96	4a	6	13	6	15	0.5330	2.68	>95.0
	97	4a	6	15	6	15	0.1813	0.68	<95.0
	98	4b	14	9	8	15	0.3929	1.68	<95.0
	99	4b	14	11	8	15	0.1732	0.64	<95.0
	100	4b	14	13	8	15	0.6625	4.26	>99.9
	101	4b	14	15	8	15	0.3920	1.67	<95.0
	102	5a	6	9	10	15	0.5116	2.50	>95.0
	103	5a	8	11	10	13	0.0846	0.22	<95.0
	104	5a	7	13	10	14	0.4824	2.18	=95.0
	105	5a	9	15	10	13	0.5343	2.48	>95.0
	106	5b	14	9	12	14	0.6923	4.61	>99.9
	107	5b	15	11	12	13	0.4299	1.75	<95.0
	108	5b	14	13	12	14	0.6187	3.47	>99.0
	109	5b	16	15	12	13	0.7266	5.11	>99.9
	110	6a	8	9	14	7	0.4107	33.00	<95.0
	111	6a	6	11	14	9	0.8667	9.21	>99.9
	112	6a	6	13	14	9	0.4167	1.33	<95.0
	113	6a	7	15	14a	7	0.6161	21.50	<95.0
	114	6b	17	9	16	7	0.3125	38.50	<95.0
	115	6b	14	11	16	9	0.4292	1.39	<95.0
	116	6b	15	13	16	8	0.0952	76.00	<95.0
	117	6b	16	15	16	6	0.5429	16.00	<95.0

[Notes to Table 16]

§ The Spearman rank correlation coefficient r_S is calculated by the formula

$$r_S = 1 - \frac{6\sum_{i=1}^{N}(u_i - v_i)^2}{N(N^2-1)}$$

where N = the number of samples in the trial; u = rank by one measurement; v = rank by another measurement; and u_i and v_i are the ranks resulting from the correlations. When evaluations agree, r_S approaches the value +1.000 through both measurement series.

*P is equivalent to the value of chi square for df = N - 1.[17]

Table 17

Summary of correlations between variables before and after aging

	Unaged control	Aging conditions: 50°C, 65% RH 305 h	50°C, 65% RH 750 h	65°C, 65% RH 305 h	65°C, 65% RH 750 h	80°C, 65% RH 305 h	80°C, 65% RH 750 h	95°C, 85% RH 305 h	95°C, 85% RH 750 h
Tensile strength after folding	***	***	***	***	***	***	***	-	-
Surface pH	***	***	***	**	***	**	***	**	*
Carboxyl groups	***	***	***	***	***	***	***	-	-
Kappa number	***	***	***	***	***	***	***	***	***
Alkali solubility	***	***	***	***	***	***	***	-	-

Level of confidence: *** 99.9% * 95% ** 99% - <95%

Table 18

Summary of correlations between a) initial tensile strength after folding and b) initial and post-aging values for other variables

	Unaged control	Aging conditions: 50°C, 65% RH 305 h	50°C, 65% RH 750 h	65°C, 65% RH 305 h	65°C, 65% RH 750 h	80°C, 65% RH 305 h	80°C, 65% RH 750 h	95°C, 85% RH 305 h	95°C, 85% RH 750 h
Surface pH	**	*	*	-	*	*	*	-	-
Carboxyl groups	-	-	-	-	-	-	-	*	-
Kappa numbers	**	**	**	*	**	-	-	*	-
Alkali solubility	-	-	-	-	-	**	**	-	-

Level of confidence: *** 99.9% * 95% ** 99% - <95%

Table 19

Summary of correlations between tensile strength after folding and four other variables under different aging conditions

	Unaged control	Aging conditions							
		50°C, 65% RH		65°C, 65% RH		80°C, 65% RH		95°C, 85% RH	
		305 h	750 h	305 h	750 h	305 h	750 h	305 h	750 h
Surface pH	**	**	-	-	-	*	***	-	-
Carboxyl groups	-	-	-	-	-	-	-	*	-
Kappa number	**	*	*	*	***	*	**	-	-
Alkali solubility	-	-	-	-	*	***	-	-	

Level of confidence: *** 99.9% * 95% ** 99% - <95%

Figures

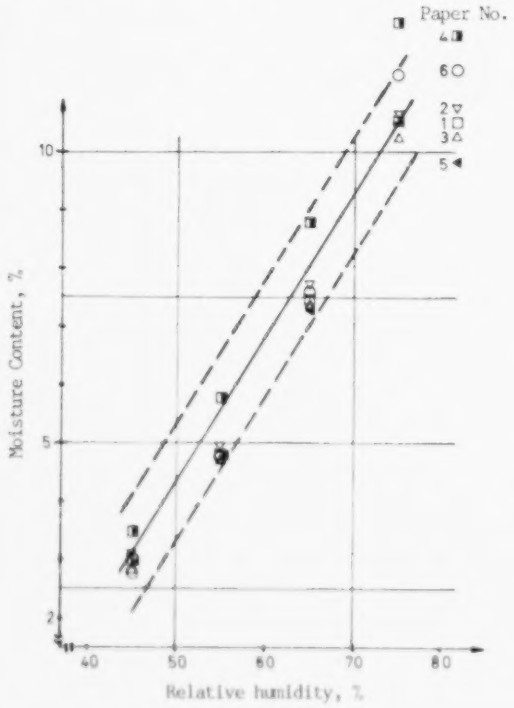

Fig. 1. Absorption of moisture by selected papers at 50°C.

The solid lines in Figures 1-4 are the regression lines, and the dotted lines indicate the general range of values.

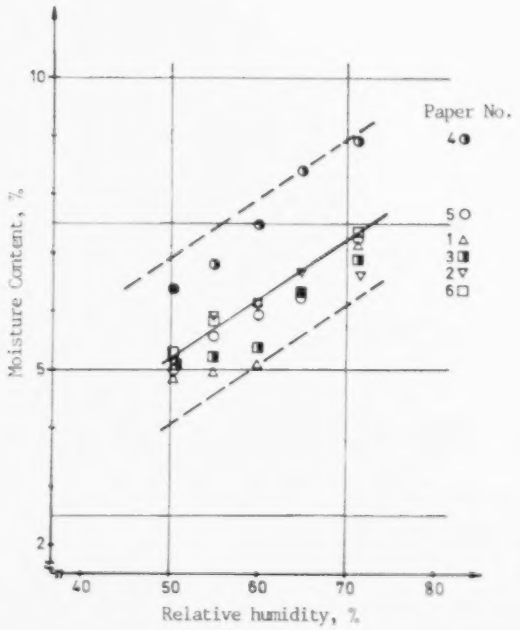

Fig. 2. Absorption of moisture by selected papers at 65°C.

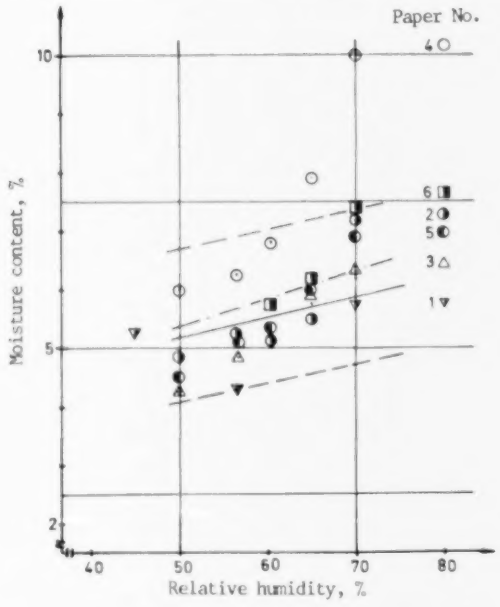

Fig. 3. Absorption of moisture by selected papers at 80°C. The dot-and-dash line shows the regression for the 14 naturally aged papers, omitting Samples 1-4.

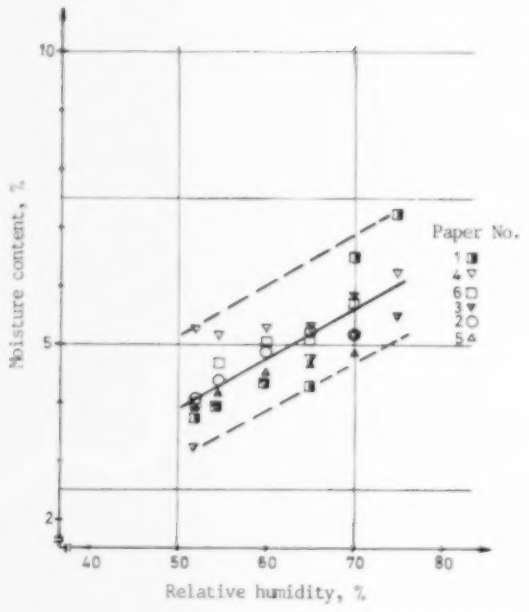

Fig. 4. Absorption of moisture by selected papers at 95°C.

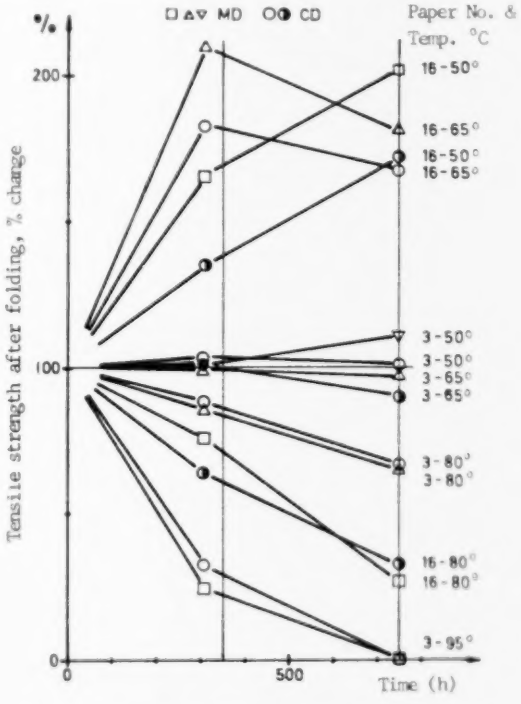

Fig. 5. Change in strength of Papers 3 and 16 after aging under various conditions. The two aging periods used are 305 and 750 hours.

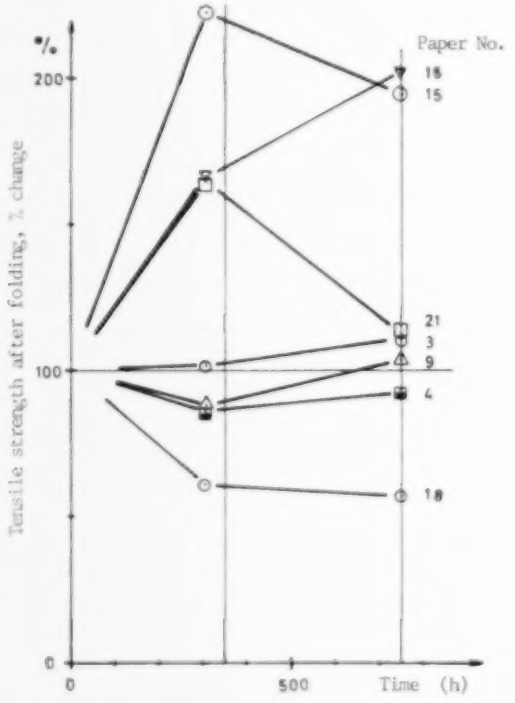

Fig. 6. Change in MD strength of selected papers aged at 50°c and 65% RH (%).

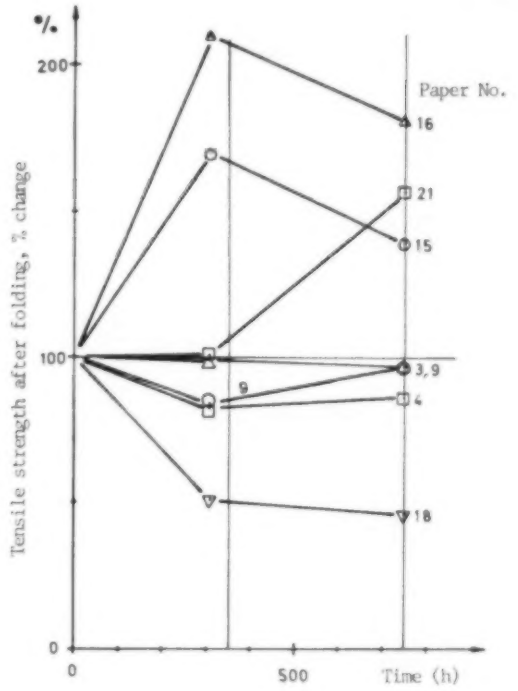

Fig. 7. Change in MD strength of selected papers aged at 65°C and 65% RH.

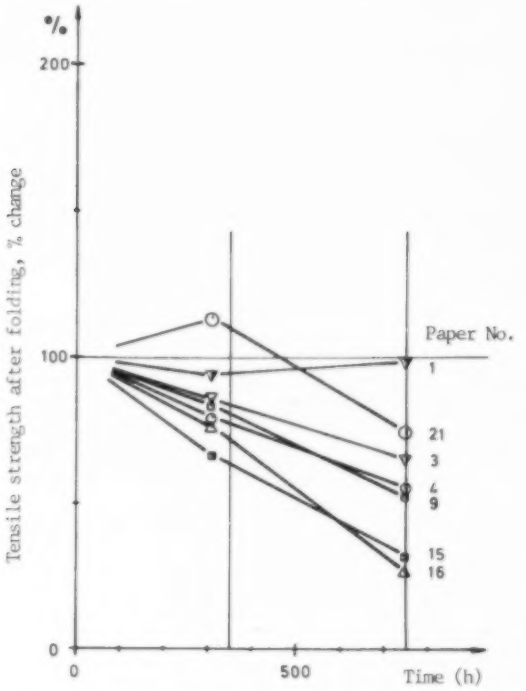

Fig. 8. Change in MD strength of selected papers aged at 80°C and 65% RH.

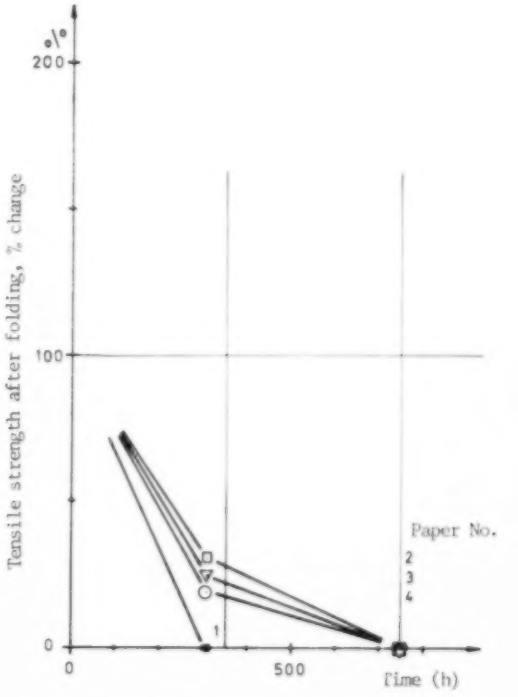

Fig. 9. Change in MD strength of selected papers aged at 95°C and 85% RH.

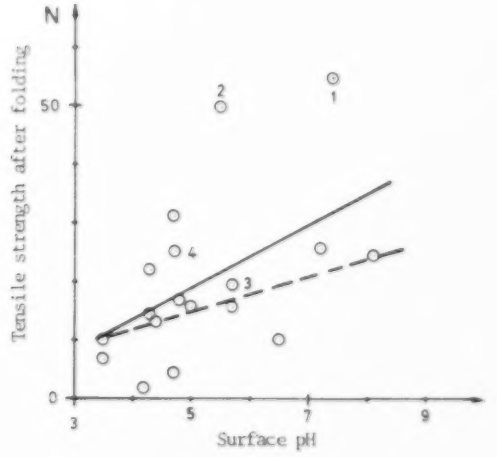

Fig. 10. Post-aging correlation between surface pH and tensile strength (average, MD + CD) after folding. The dashed line shows the regression for the 14 naturally aged papers, omitting Samples 1-4.

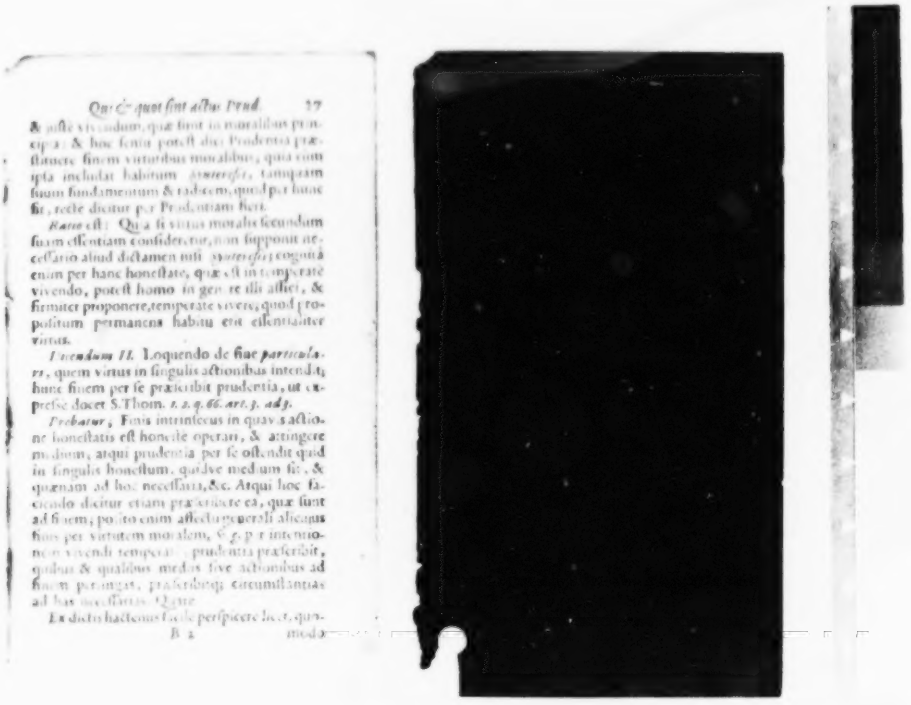

Fig. 11. Rag paper from the early 16th century, before and after artificial aging at 95°C, 85% RH, 750 h.

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Abbey Newsletter Monographic Supplement #1, 1989.
Editor: Ellen McCrady. Publisher: Abbey Publications.
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